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# Sertifikaat

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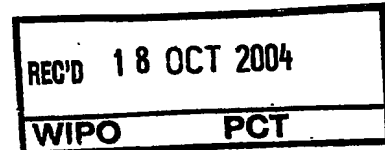
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# Certificate

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1. South African Provisional Patent Application No. **2004/2497** accompanied by a Provisional Specification was originally filed at the South African Patent Office on **30 March 2004**, in the name of **RAND AFRIKAANS UNIVERSITY** in respect of an invention entitled: **"GROUP 1-111-V1 QUARTERNARY OR HIGHER ALLOYS"**.
2. The photocopy attached hereto is a true copy of the provisional specification and drawings filed with South African Patent Application No. **2004/2497**.

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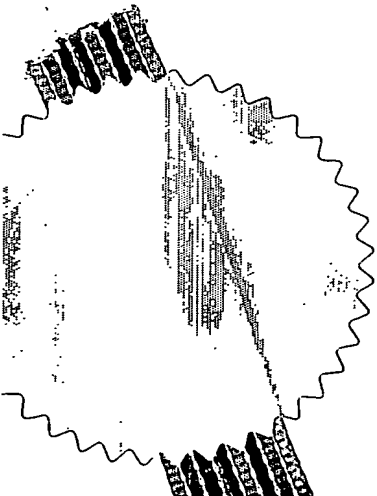
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PATENTS ACT, 1978

## REGISTER OF PATENTS

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APPLICANTS SUBSTITUTED :

DATE REGISTERED

71

ASSIGNEE(S)

DATE REGISTERED

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FULL NAME(S) OF INVENTOR(S)

72 ALBERTS, Vivian

PRIORITY CLAIMED

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DATE

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32

TITLE OF INVENTION

54

GROUP I-III-VI QUARTERNARY OR HIGHER ALLOYS

ADDRESS OF APPLICANT(S) / PATENTEE(S)

Cnr. Kingsway & University Road  
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2006  
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REF

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61

FRESH APPLICATION BASED ON

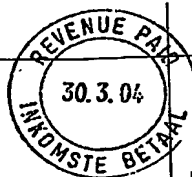
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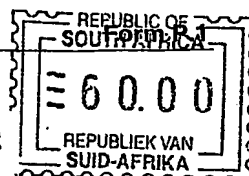
**APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT**

(Section 30 (1) - Regulation 22)

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate.



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<b>FULL NAME(S) OF APPLICANT(S)</b>	
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<b>TITLE OF INVENTION</b>	
54	GROUP I-III-VI QUATERNARY OR HIGHER ALLOYS
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<b>THIS APPLICATION IS ACCOMPANIED BY :</b>		
x	1a	A single copy of a provisional specification of 32 pages.
	1b	Two copies of a complete specification of pages.
	2a	Informal drawings of sheets.
x	2b	Formal drawings of 15 sheets.
	3	Publication particulars and abstract (form P8 in duplicate).
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	8	Assignment of priority rights.
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	10	A declaration and power of attorney on form P3.
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	12	Request for classification on form P9.
	13a	Request for delay of acceptance on form P4.
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**DATED** 30 March 2004

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REC 2004-03-30
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## REPUBLIC OF SOUTH AFRICA

## PATENTS ACT, 1978

PROVISIONAL SPECIFICATION  
( Section 30 (1) - Regulation 27 )

OFFICIAL APPLICATION NO.		LODGING DATE	DMK REFERENCE
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FULL NAME(S) OF APPLICANT(S)			
71	RAND AFRIKAANS UNIVERSITY		
FULL NAME(S) OF INVENTOR(S)			
72	ALBERTS, Vivian		
TITLE OF INVENTION			
54	GROUP I-III-VI QUARTERNARY OR HIGHER ALLOYS		

## Group I-III-VI quaternary or higher alloys.

### Field of the invention

5 THIS invention relates to group I-III-VI quaternary or higher alloys suitable for use as semiconductor films. More particularly, but not exclusively, this invention relates to homogenous quaternary and pentenary alloys suitable for use as semiconductor films.

### 10 Background to the invention

For the purposes of this specification the term "pentenary alloy" refers to an alloy having 5 different elements. So for example,  $\text{Cu}(\text{In}, \text{Ga})(\text{S}, \text{Se})_2$  is a pentenary alloy wherein the 5 different  
15 elements are copper (Cu), indium (In), gallium (Ga), selenium (Se) and sulfur (S). Similarly the term "quaternary alloy" refers to an alloy having 4 different elements. Likewise, a ternary alloy has three different elements and a binary alloy has two different elements.

20 For the purposes of this specification, the term "homogeneous" alloy or semiconductor film means that the different elements constituting the alloy are distributed homogeneously through the alloy such that the alloy has a constant lattice parameter and  
25 band gap value throughout.

Furthermore, for purposes of this specification, a "heterogeneous" quaternary, pentenary alloy or semiconductor film means that means that the alloy comprises discrete stable ternary phases  
30 (e.g.  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$ ) with a resultant abrupt change in the lattice parameter and band gap value along the thickness of the alloy.

Still further, for purposes of this specification a "graded" quaternary, pentenary alloy or semiconductor film means that the atomic concentration of the respective elements varies continuously with sample depth, resulting in a compositionally  
5 graded alloy (e.g.  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  where the value of  $x$  varies continuously), which results in a continuous variation in the lattice parameters and band gap value along the thickness of the alloy.

10 Crystalline and multi-crystalline silicon is to date the primary material used in the production of solar modules/photovoltaic cells. The main problem associated with this material is the high cost of manufacturing. In an effort to reduce fabrication costs and increase material utilization, semiconductor thin film alloys have  
15 been the subject of intensive research. In this regard, group I-III-VI alloys, such as  $\text{CuInSe}_2$ ,  $\text{CuGaSe}_2$  and  $\text{CuInS}_2$ , are promising candidates for absorber layers in thin film photovoltaic cells or devices.

20 Of particular interest are semiconductor films comprising group I-III-VI alloys wherein the alloy includes Ga in combination with another group III element, since the presence of Ga in such films results in absorber films with higher band gap values and subsequently, in solar/photovoltaic cell devices, with higher open-  
25 circuit voltages and reduced short circuit currents. Of even greater interest are semiconductor films comprising pentenary alloys (pentenary alloy semiconductor films).

30 In respect of semiconductor films comprising pentenary alloys having  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{Se}_{1-y}\text{S}_y)_2$  as a general formula, the band gap can be shifted systematically between 1.0 and 2.4eV in order to achieve an optimum match with the solar spectrum. Optimization of this material system has already resulted in laboratory-scale solar cell devices with conversion efficiencies exceeding 18%.

Without wishing to be bound by theory, a common method to produce quaternary or pentenary alloys is the traditional two step growth technique which involve (i) depositing of metallic thin films onto a substrate and (ii) the selenization and/or sulfurization of the metallic thin films in an Se and/or S containing atmosphere. These techniques are disclosed in an article by V. Alberts, J.H. Schön, and E. Bucher, Journal of Appl. Phys. **84**(12), 1998, 6881 and by A. Gupta and S. Isomura, Sol. Energy Mater. Sol. Cells **53**, 1998, 385.

A seemingly insurmountable disadvantage with traditional two-step growth techniques is that the resultant films are heterogeneous. Without wishing to be bound by theory, and solely for the purposes of background, the selenization of thin film metallic precursors such as Cu, In and Ga results in the formation of the binary selenides such as CuSe, InSe and Ga<sub>2</sub>Se<sub>3</sub>. The difference in the reaction rates between the binary selenides inevitably results in (i) discrete, ternary alloys such as CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>, therefore providing a semiconductor film including a heterogeneous alloy or (ii) a graded structure.

Typically, these prior art conditions involve the reactive annealing of the metallic thin film containing Cu, In and Ga in a selenium-containing atmosphere at a single temperature of around 500°C, resulting in:

(a) segregated semiconductor films wherein the semiconductor film comprises two layers of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> ternary alloys (where the metallic film is slowly heated over a period of 20 minutes or longer to the reaction temperature, followed by annealing in H<sub>2</sub>Se for at least 60 minutes); or

(b) a semiconductor film having a significant degree of inter-diffusion such that the Ga is graded throughout the film, the concentration of Ga increasing from the surface of the film towards the substrate (where the metallic film is heated rapidly within 5 minutes to the reaction temperature, followed by annealing in  $H_2Se$  for at least 60 minutes).

The open-circuit voltages ( $V_{oc}$ ) and short circuit currents ( $J_{sc}$ ) of solar modules/photovoltaic cells are directly related to the band gap of the semiconductor material. In the case of  $CuInSe_2$  with a low band gap value of 1 eV, the  $V_{oc}$  values are typically limited to 500 mV, while values close to 1000 mV can be achieved using a  $CuGaSe_2$  absorber layer with a higher band gap value of 1.65 eV.

In the case of segregated or graded film structure with most of the gallium residing at the back of the film, the absorber film exhibits a low band gap value in the active region of the photovoltaic cell, which ultimately limits the  $V_{oc}$  of the device. In addition, in the case of extreme grading, lattice mismatches within the graded absorber films introduce electrically active structural defects, which negatively impact on the device performance.

Once a heterogeneous  $Cu(In,Ga)Se_2$  alloy is formed by the traditional two step process and in order to increase the band gap in the near-surface region of the absorber, films are commonly reacted with  $H_2S$ . Present industrial processes include a post-sulfurization step in which a certain fraction of the selenium species in the top surface region of the film are replaced with sulfur. (See the articles by K. Kushiya, M. Tachiyuki, T. Kase, I. Sugiyama, Y. Nagoya, D. Okumura, M. Satoh, O. Yamase, and H. Takeshita, Sol. Energy Mater. Sol. Cells **49**, 1997, 277; and R. Gay, M. Dietrich, C. Fredric, C. Jensen, K. Knapp, D. Tarrant and D. Willett, Proceedings of the International Conference on E.C.



Photovoltaic Solar Energy, Vol. 12(1), 1994, 935.). This approach ultimately results in the formation of a thin  $\text{Cu(In,Ga)Se}_2$  surface layer on the graded  $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$  structure. The surface layer has an abrupt grading and the depth into the  $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$  structure is in the order of 50 nm.

The disadvantages of this standard two-step growth process which is already apply on an industrial scale, are (i) the slow exchange process between the selenium and sulfur in these films, (ii) it achieves only a slight increase in the open-circuit voltages of solar cell devices, (iii) high temperatures and long reaction times of between 90 to 120 minutes are required to achieve significant degrees of S incorporation, which ultimately increases the costs of the production process and (iv) the resulting alloys are heterogeneous, which prohibit effective control over the lattice parameters and band gap values.

It has also been demonstrated, in an article by M. Marudachalam, H. Hichri, R. Klenk, R.W. Birkmire, W.N. Schfarman and J.M. Schultz, Appl. Phys. Lett. 67(26), 1995, 3978, that  $\text{Cu(In,Ga)Se}_2$  thin films with improved homogeneity can be produced by the in-situ annealing a phase-separated mixture of  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  in argon in the temperature range of 500°C to 600°C for 60 to 120 minutes. However, Auger profiling of these specific alloys still revealed substantial variations in the In and Ga concentrations with depth. In addition, this post-annealing step in an inert atmosphere resulted in substantial losses of Se from the film, which necessitated a second annealing step in  $\text{H}_2\text{Se/Ar}$ . The additional post-annealing steps in an inert atmosphere as well as  $\text{H}_2\text{Se/Ar}$  not only compromise the reproducibility of the process, but also makes it commercially unviable.

In another attempt to produce homogeneous pentenary alloys, a complex single-stage technique has been developed. In this technique, disclosed in an article by I.M. Kötschau, H. Kerber, H. Wiesner, G. Hanna and H.W. Schock, Proceedings of the 16<sup>th</sup> European Photovoltaic Solar Energy Conference, 1-5 May 2000, Glasgow, UK, pp 724-727, all the elements (Cu, In, Ga, Se and S) are co-evaporated at constant fluxes in high vacuum from individual sources.

10 This technique allows for the controlled incorporation of gallium and sulfur into the films and hence in a decrease in the lattice parameters of the alloys. The subsequent increase in the band gap values of the pentenary alloys ultimately resulted in an increase in the open-circuit voltages of completed solar cell devices. However, glancing incident angle x-ray diffraction (GIXRD) at incident angles between 0.4° and 5° revealed a significant shift in the lattice parameters between the surface and the bulk of the material. The authors attributed this phenomenon to a copper depletion at the surface of the layer, which confirmed that the alloys were compositionally graded rather than homogeneous.

### **Object of the Invention**

25 It is an object of the invention to provide a novel pentenary and quaternary alloy which alloys are homogeneous.

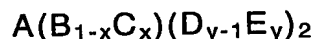
It is a further object of the invention to provide novel homogeneous quaternary and pentenary alloys suitable for use as semiconductor thin films, whereby the use of such alloys at least partially minimises the associated disadvantages in respect of thin film semiconductors comprising heterogeneous alloys.

30

## Disclosure of the Invention

According to the present invention there is provided a novel homogeneous pentenary alloy having the general formula:

5



wherein:

A is a group IB element

10 B is a group III element

C is a group III element which is different to B;

D is a group VI element;

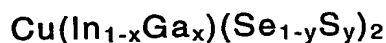
E is a group VI element which is different to D;

x may vary between 0.1 to 1.0; and

15 y may vary between 0.01 to 1

In one embodiment of the invention, A may be Cu, B may be In, C may be Ga, D may be Se and E may be S.

20 Preferably the pentenary alloy has the formula:



In another embodiment of the invention, B may be Al.

25

In a preferred embodiment of the invention, x may vary between 0.25 to 0.3 and y may vary between 0.05 to 0.5.

30 The homogeneous pentenary alloy according to the invention preferably has constant lattice parameters from the surface of the alloy to the bulk material thereof, thereby indicating that elements A, B, C, D and E are uniformly dispersed throughout the alloy.

Preferably, the homogeneous pentenary alloy has a lattice mismatch of less than 0.5%.

5 According to a second aspect of the invention, there is provided a homogeneous pentenary alloy, the homogeneous pentenary alloy being characterised in that it has a symmetric [112] diffraction peak.

10 In one embodiment of the invention, the homogeneous pentenary alloy has a symmetric [112] peak of between  $26.9^\circ$  to  $28^\circ$ , preferably between  $27.0^\circ$  to  $27.5^\circ$ .

15 The homogeneous pentenary alloy may further be characterised in that its band gap may be continuously shifted between 1 eV to 2.4 eV, preferably between 1.1 eV to 1.5 eV.

20 In a preferred embodiment of the invention, the atomic ratio of S to Se + S, i.e. the sulphur content expressed by  $S/(Se+S)$ , lies between 0.1 to 0.5.

According to a third aspect of the invention, there is provided the use of a homogeneous pentenary alloy as a semiconductor film.

25 Preferably, the homogeneous pentenary alloy according to the invention is used as a semiconductor film for a photovoltaic/solar cell.

The semiconductor film comprising the homogeneous pentenary alloy may have a thickness of  $1.5\mu\text{m}$  to  $2.0\mu\text{m}$ .

30 In an embodiment of the invention the photovoltaic/solar cell may have a conversion efficiency of between 8 to 14%, which

conversion efficiency is related to the band gap of the homogeneous pentenary alloy.

According to a fourth aspect of the present invention there is provided a novel homogeneous quaternary alloy having the general formula:



wherein:

A is a group IB element

B is a group III element

C is a group III element which is different to B, or is a group VI element;

D is a group VI element which is different to C when C is a group VI element;

x may vary between 0 and 1

In one embodiment of the invention, A may be Cu, B may be In, C may be Ga and D may be Se.

Preferably the quaternary alloy has the formula:



25

In another embodiment of the invention, C may be Se and D may be S so that the quaternary alloy has the general formula  $Cu(In,Se)S_2$ .

30 In a preferred embodiment of the invention, x may vary between 0.25 to 0.3.

The homogeneous quaternary alloy according to the invention preferably has constant lattice parameters from the surface of the

alloy to the bulk material thereof, thereby indicating that elements A, B, C and D are uniformly dispersed throughout the alloy.

5 Preferably the quaternary alloy has a lattice mismatch of less than 0.0002%.

10 According to a fifth aspect of the invention, there is provided a homogeneous quaternary alloy, the homogeneous quaternary alloy being characterised in that it has a symmetric [112] diffraction peak.

15 In one embodiment of the invention, the homogeneous quaternary alloy has a symmetric [112] peak of between  $26.8^{\circ}$  to  $27.0^{\circ}$ , preferably between  $26.85^{\circ}$  to  $26.9^{\circ}$ .

20 The homogeneous quaternary alloy may further be characterised in that its band gap may be shifted between 1.1 eV to 1.2 eV, preferably between 1.15 eV to 1.18 eV.

25 In a preferred embodiment of the invention, the atomic ratio of Ga to Ga + In, i.e. the gallium content expressed by  $\text{Ga}/(\text{Ga}+\text{In})$ , lies between 0.25 to 0.3.

30 According to a sixth aspect of the invention, there is provided the use of a homogeneous pentenary alloy as a semiconductor film.

Preferably, the homogeneous quaternary alloy according to the invention is used as a semiconductor film for a photovoltaic/solar cell.

30

The semiconductor film comprising the homogeneous quaternary alloy may have a thickness of  $1.5\mu\text{m}$  to  $2.0\mu\text{m}$ .

In an embodiment of the invention the photovoltaic/solar cell may have a conversion efficiency of between 8 to 14%, which conversion efficiency is related to the band gap of the homogeneous quaternary alloy.

5

According to a seventh aspect of the invention, there is provided a semiconductor film comprising a homogeneous pentenary alloy or quaternary alloy as described above.

10 According to yet a further aspect of the invention, there is provided a photovoltaic/solar cell including a semiconductor film comprising a homogeneous pentenary alloy or quaternary alloy as described above.

## 15 Detailed Description of the Invention

Without thereby limiting the scope of the invention and by means of example only embodiments of the invention will now be described by means of the following examples. In the examples  
20 reference is made to the accompanying figures:

Figures 1.1 - 1.2 are X-ray diffraction spectra (Cu  $K_{\alpha}$  radiation) of the first film formed according to step ii of example 1. More particularly figure 1.1 is an XRD pattern of the first film of sample 200250-a and figure 1.2 is an XRD pattern of the first film of sample 200251-a;

Figure 2 are X-ray diffraction spectra (Cu  $K_{\alpha}$  radiation) depicting the crystalline nature of the resultant second film of sample 200251-a, which were formed according to steps iii

and iv of example 1, illustrating the transitions from the ternary to the quaternary and pentenary alloy states;

Figures 3.1-3.2.

are GIXRD patterns of the [112] peak positions of the homogeneous pentenary alloys of samples 200251-a and 200250-a in comparative example 1, measured with Cu  $K_{\alpha}$  radiation;

Figure 4

is a plot of open-circuit voltage ( $V_{oc}$ ) for a number of photovoltaic cells having semiconductor absorber films of sample 200251-a as set out in example 2;

Figure 5

is an XRD of the pentenary alloy of Example 3;

Figure 6

is a Quantum Efficiency (QE) graph of the pentenary alloy of Example 3;

Figure 7

Are XRD patterns of homogeneous  $Cu(In_{0.75}Ga_{0.25})(Se_{0.95}S_{0.05})_2$ ;  $Cu(In_{0.75}Ga_{0.25})(Se_{0.75}S_{0.25})$  and  $Cu(In_{0.75}Ga_{0.25})(Se_{0.6}S_{0.4})_2$  formed according to the steps set out in Example 1.

Figure 8

is a Quantum Efficiency (QE) graph of a homogeneous  $Cu(In_{0.75}Ga_{0.25})(Se_{0.8}S_{0.2})_2$  alloy, prepared according to the steps set out in Example 1.



- Figures 9 Plot of band gap values as function of S/Se+S ratio for a series of homogeneous pentenary alloys, prepared according to the steps set out in Example 1.
- Figures 10-12 are SEM micrographs depicting the surface morphology of homogeneous  $\text{Cu}(\text{In}_{0.75}\text{Ga}_{0.25})(\text{Se}_{0.8}\text{S}_{0.2})_2$ ,  $\text{Cu}(\text{In}_{0.75}\text{Ga}_{0.25})(\text{Se}_{0.6}\text{S}_{0.4})_2$  and  $\text{Cu}(\text{In}_{0.75}\text{Ga}_{0.25})(\text{Se}_{0.8}\text{S}_{0.2})_2$  pentenary alloys.
- Figure 13.1-13.2 are XRD patterns (Cu  $K_\alpha$  radiation) of a graded quaternary alloy of comparative example 2 and a homogeneous quaternary alloy of comparative example 2;
- Figure 14 are GIXRD patterns of the [112] peak position of the homogeneous quaternary alloy of comparative example 2. The correspondence in the lattice parameters as function of sample depth indicates that the film is homogeneous rather than compositionally graded;
- Figure 15.1-15.2 are X-ray fluorescence profiles depicting the in-depth composition properties of the graded quaternary alloy and homogeneous quaternary alloy of comparative example 2 respectively.

## General Experimental Procedure

It is well known to those skilled in the art that photovoltaic cells include a substrate for supporting a semiconductor film. Typically, any suitable substrate may be used, which substrate does not react with the semiconductor film and which does not modulate the semiconductor properties. Suitable substrates include glass, flexible metallic or polymer foils and the like.

The substrate may have a thickness of 0.05 to 3.0 mm and is often coated with a metal layer of molybdenum in order to enhance the adhesion of a resultant semiconductor film to the substrate and to serve as a contact in a completed photovoltaic device.

The thickness of the Mo coating is usually between 0.5 to 1.0  $\mu\text{m}$  and is deposited onto the substrate by DC magnetron sputtering at a working pressure of between 0.1 to 0.8 Pa. It will be appreciated that there are many other techniques known in the art which relate to the use and deposition of metal layers, for example there may be more than one layer, or chromium may be used in place of molybdenum.

### *Step (i)*

For purposes of the experiment, a 2 mm thick soda lime glass substrate was used. The substrate was cleaned in an ultrasonically stirred soap solution for 10 minutes by gently moving the substrate placed in a holder. The substrate was then held under a cold deionised water tap for a few minutes to ensure the removal of excess soap thereon. Thereafter, the substrate was cleaned in an ultrasonically stirred deionised hot water bath by gently moving the substrate holder. Finally, the substrate was

dried for 10 minutes in dry-nitrogen in an oven maintained at 120°C.

Once dried, a Mo layer was deposited onto the substrate. This was followed by co-sputtering the metal film of Cu, Ga and In onto the Mo layer. The deposition of Mo and the co-sputtering were carried out in a DC magnetron sputtering unit consisting of a deposition chamber which accommodates three 9 inch circular cathodes (targets): Mo, pure In and a  $\text{Cu}_{0.75}\text{Ga}_{0.25}$  alloy target.

The deposition chamber was evacuated to a base pressure of  $5 \times 10^{-5}$  Pa for at least three hours. The Mo layer was deposited without any intentional heating of the substrate at a working pressure of 0.5 Pa, using Ar as plasma gas. The total thickness of the Mo layer was 1  $\mu\text{m}$ .

The deposition of the Mo layer was followed, without breaking vacuum, by the co-sputtering of  $\text{Cu}_{0.75}\text{Ga}_{0.25}$  and In at a working pressure of 0.3 Pa. The co-sputtering was also carried out without intentional substrate heating and the substrate was rotated during co-sputtering in order to enhance the mixing of the Cu-Ga-In alloy. The total thickness of the Cu-In-Ga alloys was 0.6  $\mu\text{m}$  and the Cu/(In+Ga)- and Ga/(Ga+In)- atomic ratios were maintained at 0.9 and 0.25 respectively.

#### Example 1: Experimental procedure for the production of a group I-III-VI pentenary alloy

##### *Step ii*

The substrate with the co-sputtered metal film of step i was placed in a horizontal quartz tube reactor (herein after referred to as the reactor tube). The substrate was laid on a graphite

substrate holder and placed in the reactor tube. Graphite substrate holders were used to ensure the uniform heating of the substrate.

- 5 The reactor tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two hours before carrying out step ii. The reaction tube was then pressurised and a constant Ar flow of 1300 standard cubic centimetres per minute (hereinafter referred to as sccm) was established and maintained during the reaction process.

10

Once a constant inert gas flow was established, the temperature of the substrate with the metal film was ramped up to the reaction temperatures set out in Table 1 below over a period of 5 minutes.

- 15 The reaction gas mixture (0.06 molar %  $\text{H}_2\text{Se}$  in Ar) was passed through the reactor tube while the substrate was heated to the reaction temperatures set out in Table 1 for the reaction periods also set out in Table 1 so as to form a first film comprising a stable mixture of binary selenides, namely  $\text{CuSe}$ ,  $\text{InSe}$  and
- 20  $\text{Ga}_2\text{Se}_3$  and at least one of the following ternary alloys, namely  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$ . The presence of one or both of the ternary alloys is dependent upon the reaction temperature of step ii.

- 25 Referring to figure 1.1 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1 for sample 200250-a, it is clear that there is present a mixture of the three binary selenides and  $\text{CuInSe}_2$ . Under the reaction conditions for sample 200250-a, there is no evidence of the
- 30 formation of  $\text{CuGaSe}_2$  at  $400^\circ\text{C}$ .

Referring to figure 1.2 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1

below for sample 200251-a, reflections [112], [220/204] and [312/116] comprise (a) relatively sharply defined peak positions corresponding to  $\text{CuInSe}_2$  and (b) shoulders resulting from the presence of  $\text{CuGaSe}_2$  and the remaining binary selenides of  $\text{CuSe}$  and  $\text{Ga}_2\text{Se}_3$ .

Upon the termination of the reaction periods as set out in Table 1, the samples were subjected to a treatment step in order to further maintain the stability of the resultant stable mixture. This was done by terminating the flow of  $\text{H}_2\text{Se}$  in the reaction tube and by rapidly cooling the samples to temperatures of below  $100^\circ\text{C}$ . The samples were kept under the above conditions for 15 minutes to ensure the complete removal of the  $\text{H}_2\text{Se}$  species from the reactor tube.

Both figures 1.1 and 1.2 depict a stable mixture wherein the reaction conditions set out in Table 1 below prevent the reaction going to completion and thus forming fully reacted ternary alloys of  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  in the absence of  $\text{CuSe}$ ,  $\text{InSe}$  and  $\text{Ga}_2\text{Se}_3$ .

It is believed by the inventor that starving the system of Se by using extremely low concentrations of Se, and by using low temperatures so as to prevent the completion of the selenization reaction to form fully reacted ternary alloys, stable mixtures such as those represented in figures 1.1 or 1.2 can be achieved.

Table 1: Reaction conditions (temperature and time) for step ii according to the invention.

Sample	Reaction conditions (H <sub>2</sub> Se/Ar)
200248-c	400°C/20min
200250-a	400°C/30min
200263-a	400°C/40min
200371-a	400°C/60min
200251-a	450°C/30min

5

### Step iii

10 The first film of step ii formed under the reaction conditions in Table 1 above was then heated in the reaction tube in an atmosphere containing a mixture of H<sub>2</sub>S and Ar (the molar percentage of S in the reactive mixture being maintained close to 0.35% relative to Ar) at a reaction temperature of 450°C for a period of 5 minutes such that the binary selenides react with S to  
15 convert the first film of step ii into a second film comprising a mixture of sulfoselenides, namely Cu(Se,S), In(Se,S) and Ga(Se,S) and the ternary alloys.

20 Referring to Figure 2 which is a XRD pattern of sample 20051-a, and in particular the XRD for step iii, the presence of In(Se,S) is visible, however the remaining sulfoselenides of Cu(Se,S) and Ga(Se,S) are not shown in the selected 2θ range. The inventor believes that at temperatures around 450°C, and as depicted in the XRD for step iii, the reaction between the existing S species  
25 in the gaseous atmosphere and the ternary alloys (indicated by peaks 1 at 26.71° and 2 at 27.75° in fig. 2) is substantially

insignificant. In other words, the reaction between S and the ternary alloys is insignificant at this specific temperature.

*Step iv*

5

The second film of step iii was then subjected to the following heat treatment steps in the reaction tube:

10

(a) annealing the second film of step iii at temperatures of about 500°C for 5 minutes, such that the sulfoselenides react with the ternary alloys to produce quaternary  $\text{CuIn}(\text{Se},\text{S})_2$  and  $\text{CuGa}(\text{Se},\text{S})_2$  alloys (indicated by peaks 3 at 27.01° and 4 at 28.05° in the XRD for step iv(a)).

15

20

It is believed by the inventor that in the event that step ii is carried out at 400°C, and thus in the absence of  $\text{CuGaSe}_2$ , the sulfoselenides may directly react to form  $\text{CuGa}(\text{Se},\text{S})_2$  in this step. However, under the latter experimental conditions the resulting quaternary alloy will contain a higher S concentration, resulting in a shift of peak 4 to a higher  $2\theta$  value than that indicated in the XRD pattern for step iv(a).

25

The reaction of S with the group I-III-VI<sub>2</sub> ternary alloys is represented by the absence of the sulfoselenides for example, the absence of the  $\text{In}(\text{Se},\text{S})$  peak in the XRD pattern for step iv(a) in figure 2 is indicative of the fact that it has reacted with  $\text{CuInSe}_2$  to form  $\text{CuIn}(\text{Se},\text{S})_2$ .

30

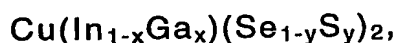
Comparing the XRD for step iii in figure 2 with the XRD for step vi(a) in figure 2, it is clear from the subsequent  $2\theta$  shift that the ternary alloys (represented by [112] peaks 1 and 2) have reacted with the sulfoselenides to form the

quaternary alloys  $\text{CuIn}(\text{Se},\text{S})_2$  and  $\text{CuGa}(\text{Se},\text{S})_2$  (represented by [112] peaks 3 and 4).

The degree of shift of the [112] peak from position 1 to 3, and 2 to 4, is determined by the volume fraction of sulfoselenides available to react with the ternary alloys. The volume fraction sulfoselenides is in turn dependent on the volume fraction binary selenides present in the first film of step ii. Once the stable fully reacted quaternary alloys are formed around  $500^\circ\text{C}$ , the reaction process becomes diffusion limited and further reaction to  $\text{H}_2\text{S}/\text{Ar}$  at  $500^\circ\text{C}$  for extended periods has insignificant influences on the crystalline state and S content of the composite alloy.

(b) Annealing the resultant composite alloy in the reaction tube from (a) above at a temperature of  $550^\circ\text{C}$  for a period of 15 minutes. The transition from the quaternary to pentenary alloy state (indicated by peak 5 at  $27.2^\circ$  in the XRD for step iv(b) in Fig. 2) occurs within 10 to 15 minutes of the reaction with  $\text{H}_2\text{S}$ , while an additional 15 minutes of annealing is typically required to optimize the structural properties of the pentenary alloy.

The homogeneous pentenary alloys have typical thickness of between 1.5 and 2  $\mu\text{m}$  and may be described by the chemical formula:



wherein  $x$  may vary between 0.1 and 0.5, preferably between 0.25 and 0.3 and  $y$  may be between 0 and 1, preferably between 0.05 and 0.5.



Both steps iii and iv are carried out consecutively in a reactive gas mixture of  $\text{H}_2\text{S}$ , wherein the temperature is ramped up from 450°C to 550°C.

- 5 Upon the completion of both steps iii and iv, the reaction tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two hours to ensure the complete removal of toxic gases from the reactor tube. The tube was then pressurized and the samples were removed.

10

#### Comparative Example 1 – pentenary alloys

15 The samples set out in Table 1 above were subjected to steps iii and iv to form homogeneous semiconductor pentenary alloys and their corresponding chemical compositions as determined by energy dispersive x-ray spectroscopy (EDS) with reference to  $\text{Cu}/(\text{In}+\text{Ga})$ ,  $\text{Ga}/(\text{Ga}+\text{In})$ , and  $\text{S}/(\text{Se}+\text{S})$  atomic ratios are set out in Table 2 below. Also shown in Table 2 below are the band gap values for each of the samples as well as the position of the [112] diffraction peaks.

20

Table 2: Summary of reaction conditions<sup>†</sup> and their influence on the degree of sulfur incorporation and the resulting band gap values of the respective samples.

25

Sample	Step ii reaction conditions $\text{H}_2\text{Se}/\text{Ar}$	Step iv reaction conditions $\text{H}_2\text{S}/\text{Ar}$	$\text{Cu}/\text{In}$ +Ga	$\text{Ga}/\text{Ga}+\text{In}$	$\text{S}/\text{Se}+\text{S}$	$2\theta_{(112)}$	$E_g$ (eV)
200248-c	400°C/ 20min	550°C/ 30min	0.90	0.25	0.56	27.65	1.39
200250-a	400°C/ 30min	550°C/ 30min	0.91	0.25	0.45	27.55	1.32

200263-a	400°C/ 40min	550°C/ 30min	0.90	0.25	0.32	27.30	1.23
200371-a	400°C/ 60min	550°C/ 30min	0.93	0.25	0.10	27.0	1.15
200251-a	450°C/ 30min	550°C/ 30min	0.92	0.24	0.23	27.20	1.20
200252-a	450°C/ 30min	550°C/ 90min <sup>‡</sup>	0.91	0.23	0.25	27.21	1.21

<sup>†</sup>These studies were conducted in a constant flow of 0.06% H<sub>2</sub>Se diluted in Ar and 0.35% H<sub>2</sub>S diluted in Ar. The 2 $\theta$ - positions of the [112] peaks of the pentenary alloys were measured by GIXRD with a Cu tube at 40kV. The corresponding band gap values were calculated from quantum efficiency measurements. <sup>‡</sup> The time period for step vi(b) was increased to 90 minutes.

A comparison of the first four samples in Table 2 clearly indicates the influence of the conditions of step ii of the invention on the degree of sulfur incorporation which is set out in the S/(S+Se) column of the table. Accordingly, changing the conditions of step ii modified the subsequent reaction kinetics during step iii of the invention resulting in a change in the sulfur incorporation in the final Cu(In<sub>0.75</sub>Ga<sub>0.25</sub>)(Se<sub>1-y</sub>S<sub>y</sub>)<sub>2</sub> semiconductor film.

A comparison of sample # 200250-a and # 200251-a, indicates how an increase in the reaction temperature of step ii from 400°C to 450°C led to a substantial decrease in the sulfur incorporation and hence a shift in the [112] diffraction peak to a lower angle.

In the case of the last two samples, (i.e. 200251-a and 200252-a) the reaction conditions of step ii were maintained constant, while the reaction periods for annealing the resultant composite alloy in step iv(b) above was increased from 30 to 90 minutes. Comparison of these samples clearly indicates that annealing in the presence of an H<sub>2</sub>S/Ar atmosphere for extended periods

above 30 minutes had marginal influences on the degree of sulfur incorporation.

Accordingly this indicates that the homogeneous pentenary alloy is formed after only 30 minutes of annealing in  $H_2S/Ar$  at  $550^\circ C$  therefore implying that once the fully reacted homogeneous pentenary alloys are produced, the reaction process becomes diffusion limited and further incorporation of sulfur needs to occur via the replacement of selenium species.

Figures 3.1 and 3.2 are grazing-incidence x-ray diffraction (GIXRD) patterns of the [112] reflections of samples 200251-a, 200250-a set out in Table 2 above. In this characterization method, decreasing amounts of the incident angle result in a decreasing penetration depth of the x-ray beam. It is important to note that scattering angles between  $0.2^\circ$  and  $10^\circ$  revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms the homogeneity of the pentenary alloys. Of equal significance is that the variation in the conditions of step ii resulted in a dramatic shift in the  $2\theta$ - position of the [112] diffraction peaks. Since the gallium content is virtually constant in all composite alloys, this relative shift is attributed to the varying degrees of sulfur incorporation. Table 3 below shows the various shifts.

Table 3: Summary of the positions of the [112] reflections at different angles of incidence. The overall peak shifts are calculated as the difference between the peak position of the [112] reflection at  $0.5^\circ$  (near-surface) and  $10^\circ$  (bulk) of the samples.

Sample #	S/Se+S	$2\theta_{(112)}$ (0.5°)	$2\theta_{(112)}$ (1°)	$2\theta_{(112)}$ (2°)	$2\theta_{(112)}$ (5°)	$2\theta_{(112)}$ (10°)	Overall Shift (°)
200250-a	0.45	27.547	27.548	27.548	27.502	27.499	0.048
200263-a	0.32	27.300	27.299	27.307	27.300	27.303	0.003
200251-a	0.23	27.201	27.203	27.202	27.201	27.199	0.002
200252-a	0.25	27.205	27.250	27.249	27.247	27.198	0.007

Example 2: Determination of the open-circuit voltages for various solar cell devices comprising homogeneous pentenary alloys as absorber films.

5

Solar cells devices were fabricated according to a standard cell fabrication procedure, which included a 50 nm CdS buffer layer and a 50 nm intrinsic ZnO/150 nm indium tin oxide (ITO) window layer. The glass/Mo/Cu(In,Ga)(Se,S)<sub>2</sub>/CdS/ZnO cell structures were evaluated under simulated A.M. 1.5 conditions at 25°C. The band gap values of the homogeneous pentenary alloys were varied by modifying the reaction conditions of step ii, as indicated in Table 2. The corresponding cell parameters are set out in Table 4 below.

10

15

Table 4: Summary of the cell parameters of various photovoltaic devices in which the absorber films are homogeneous pentenary alloys with different band gap values.

Samples	Ga/Ga+ In	S/Se+ S	E <sub>G</sub> eV	V <sub>oc</sub> mV	J <sub>sc</sub> mA/cm <sup>2</sup>	FF %	η %
200248-c	0.25	0.56	1.39	677.9	23.55	53.3	8.5
200250-a	0.25	0.45	1.32	685.9	27.17	59.8	11.2
200252-a	0.23	0.25	1.21	630.2	29.46	64.1	11.9
200251-a	0.24	0.23	1.20	610.4	32.86	67.5	13.5

20

The conversion efficiencies were critically related to the band gap of the pentenary alloys and varied between 8% and 14%, the best device being that with the lowest band gap (sample 200251-a). All devices had open-circuit voltages ( $V_{oc}$ ) beyond 600 mV. Also, 24 photovoltaic cells were made from pentenary alloys prepared under the reaction conditions set out above for sample 200251-a. The  $V_{oc}$  values of these cells were confined to values in the range of 600 to 640 mV (see fig. 4). This is clear evidence of the reproducibility of the method according to the invention.

Example 3: Discussion of a homogeneous pentenary alloys prepared in terms of the steps I to iv above

Figure 5 depicts the positions of the [112] diffraction peaks of a  $CuIn_{0.75}Ga_{0.3}$  precursor, which was (i) first selenized and subsequently (ii) sulfurized under the conditions and steps set out above. The experimental conditions during selenization/sulfurization were manipulated in order to produce pentenary alloys with high S content (i.e.  $S/Se+S = 0.7$ ). Peak (i) at  $26.58^\circ$  is the expected [112] peak position of  $CuInSe_2$  after selenization. The asymmetric behaviour of the peak at this stage of processing is attributed to Ga grading.

It is important to note, however, that the [112] peak position shifted to an angle of  $27.8^\circ$  after sulfurization. Using Vegard's law and assuming a Ga concentration of around 30%, this corresponds to a S content of around 60%, hence a homogeneous  $Cu(In_{0.7}Ga_{0.3})(Se_{0.3}S_{0.7})$  alloy. These compositions were confirmed by EDS measurements. It is especially important to note that peak (ii) is symmetric with no evidence of compositional broadening. The band gap of this alloy, determined from QE measurements, is 1.4 eV (see Fig 6). Although, this band gap is too high for optimum conversion efficiencies, but this example is

used to demonstrate that homogeneous material can be produced even for high S containing films.

Figure 7 depicts the [112] peak positions of various homogeneous Cu(In,Ga)(Se,S)<sub>2</sub> alloys. Once again it is assumed that the Ga concentration in precursors remains constant and the selenization/sulfurization reaction conditions were manipulated to control the degree of S incorporation, and hence the lattice parameters.

It can be seen from Fig. 7 that the position of the [112] peak varies between 26.9° to 27.4°, which corresponds to S/Se+S atomic ratios between 0.05 and 0.4. These values are again estimated from Vegard's law, assuming a homogeneous pentenary alloy. The corresponding shift in band gap value is between 1.1 eV and 1.3eV for these specific alloys. Figure 8 shows, for example, the typical QE curve for a homogeneous Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>)(Se<sub>0.8</sub>S<sub>0.2</sub>) alloy with a [112] peak position close to 27.2°. Figure 9 shows a plot of the band gap values as a function of S/Se+S ratio.

Figures 10, 11 and 12 depict the typical surface morphologies of homogeneous CIGSSe thin films with varying S content and hence band gap. In the case of Fig. 10, the position of the [112] peak is at 27.2° and the corresponding band gap is at 1.20eV (see Fig 8). The [112] peak position of the alloy in Fig. 11 is at 27.4°. Fig. 12 depicts the structural features of the alloys with a [112] peak position close to 27.8° with corresponding band gap value at 1.4eV, as shown in Fig. 6.

#### Example 4: Experimental procedure for the production of a group I-III-VI quaternary alloy

Step i is the same as set out under general experimental procedure.

5    *Step ii*

In this case the same method as set out in step ii above was followed, however the reaction temperature was kept at 400°C so as to form a first film comprising a stable mixture of binary selenides and  $\text{CuInSe}_2$  only.

It is believed by the inventor that in the case of the production of quaternary alloy semiconductor films it is necessary to prevent the formation of the second ternary alloy, namely  $\text{CuGaSe}_2$  so as to obtain a homogeneous quaternary alloy. This was achieved by keeping the reaction temperature at 400°C.

As above, the first film of step ii is subjected to a treatment step to maintain the stability of the mixture, wherein the  $\text{H}_2\text{Se}$  flow is terminated and the first film is cooled to temperatures below 100°C. The Ar flow in this case was maintained for a period of at least 15 minutes, once again to ensure the complete removal of the  $\text{H}_2\text{Se}$  species.

25    *Step iii*

In the case of the production of a quaternary alloy semiconductor film, this step is not carried out.

30    *Step iv*

The first film is subjected to the following consecutive steps:

(a) heating the first film in the reaction tube in an inert atmosphere of Ar to a reaction temperature of 500°C for 5 minutes ;

5 (b) annealing the first film in the reaction tube in an Ar containing atmosphere at 500°C for at least 15 minutes;

(c) annealing the first film in the presence of 0.06 molar percent of H<sub>2</sub>Se in Ar for 30 minutes at 500°C

10

to form a homogeneous quaternary alloy semiconductor film.

As in the case of the formation of a pentenary alloy, the reaction tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two  
15 hours to ensure the complete removal of toxic gases from the reactor tube. The tube was then pressurized and the samples were removed.

#### Comparative Example 2 – quaternary alloys

20

Figures 13.1 and 13.2 represent XRD patterns, depicting the crystalline features of a typical graded quaternary alloy and a homogeneous quaternary alloys respectively, the alloys being prepared in the manner set out below. In both cases,  
25 measurements were taken with Cu K<sub>α</sub> radiation at 40kV.

In the case of the graded quaternary alloy (see XRD pattern in Fig. 13.1), the alloy was rapidly heated in less than 5 minutes to 500°C in the presence of H<sub>2</sub>Se, followed by an annealing step in  
30 5 molar percent H<sub>2</sub>Se in Ar for 60 minutes at 500°C. This procedure resulted in a significant degree of interdiffusion between the In-rich and Ga-rich phases and XRD analysis indicated the presence of a graded CuIn<sub>x</sub>Ga<sub>1-x</sub>Se structure. This



phenomenon is represented by the asymmetric broadening of the [112], [220/204] and [312/116] diffraction peaks. In this regard it is important to note that the position of the [112] diffraction peak at  $26.65^\circ$  still represents the lattice parameters of the pure  $\text{CuInSe}_2$  phase, while the shoulder is due to increasing amounts of Ga which extend all the way to the peak position of  $\text{CuGaSe}_2$ . It is therefore reasonable to assume that the surface of the absorber film contains pure  $\text{CuInSe}_2$  and that the gallium increases gradually towards the Mo back contact.

10

The second sample, i.e. the homogeneous quaternary alloy, was prepared under the described experimental conditions set out in steps i, ii and iv for quaternary alloys. In order to control the reaction velocities of the binary selenides, step ii was carried out at  $400^\circ\text{C}$ , using extremely low gas concentrations of 0.06 molar %  $\text{H}_2\text{Se}$  in Ar. The reaction period was fixed at 30 minutes. After complete removal of Se species from the reaction zone, the first film was annealed in the presence of Ar for 15 minutes at a temperature of  $500^\circ\text{C}$ , followed immediately by an annealing step in 0.06 molar percent  $\text{H}_2\text{Se}$  in Ar for 30 minutes.

20

XRD studies of the homogeneous quaternary alloy, which is represented by Fig. 13.2, revealed that the resultant film was homogeneous with no evidence of segregated material. The sharp, well-defined chalcopyrite peaks are indicative of high crystalline quality. It is also important to note that the [112] peak position increased from about  $26.65^\circ$ , which is typical for pure  $\text{CuInSe}_2$  (as shown in Figure 13.1), to a  $2\theta$  value of  $26.95^\circ$ . The latter shift of the chalcopyrite reflection towards a larger  $2\theta$  value is in accordance with a decrease in the lattice parameter associated with an increase in Ga content in the quaternary system. This degree of shift of the diffraction peaks towards higher  $2\theta$  values is exactly in accordance with Vegard's law,

30

assuming homogeneous material and a  $\text{Ga}/(\text{Ga}+\text{In})$  atomic ratio close to 0.25.

Figure 14 depicts GIXRD patterns of the [112] peak of the homogeneous quaternary alloy at incident angles between  $0.5^\circ$  and  $10^\circ$ . Once again it should be realized that a decrease in the incident angle results in a decrease in penetration depth of the x-ray beam. It is important to note from Fig. 14 that scattering angles between  $0.5^\circ$  and  $10^\circ$  revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms that the film is uniform rather than compositionally graded.

The in-depth compositional features of the quaternary alloys were studied by x-ray fluorescence (XRF). In this characterization method, the quaternary alloys were repeatedly etched in bromine methanol, followed by XRF  $K_{\alpha 1,2}$  line intensity measurements of the remaining material after each etching step. From these analyses the chemical compositions of the graded film and homogeneous films represented in Fig 13.1. and Fig 13.2 could be estimated through almost the entire film thickness.

Figure 15.1 represents the in-depth compositional uniformity of the compositionally graded  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$  alloys film of Fig 13.1. It is important to note from Fig. 15.1 that the Cu and Se element concentrations remained virtually constant through the entire thickness of the film. Even more significant, it can be seen that the remaining material after the successive etching steps became increasingly gallium-rich, while an opposite trend was observed for indium. The resulting  $\text{Ga}/(\text{Ga}+\text{In})$  atomic ratio increased from a value of 0.28 for the sample before etching to 0.75 after the last etching step. This continuous increase in the  $\text{Ga}/(\text{Ga}+\text{In})$  atomic ratio with sample depth is consistent with the

graded  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  phase observed by the XRD studies in Fig. 13.1.

5 Figure 15.2 represents the in-depth compositional properties of the homogeneous film. It can be seen that the Cu, In, Ga and Se concentration remained virtually constant through the entire layer thickness of these specific quaternary alloys. These results are therefore in line with the XRD data presented in Fig. 13.2, confirming that this growth process eliminated the grading of  
10 gallium and indium in the  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  phase and resulted in a homogeneous quaternary alloy.

The above are only embodiments of the invention and it will be appreciated that many variations in detail are possible without  
15 thereby departing from the scope and spirit of the invention.

Dated this 30 day of March 2004

  
Patent Attorney / Agent for the Applicant

Figure 1.1

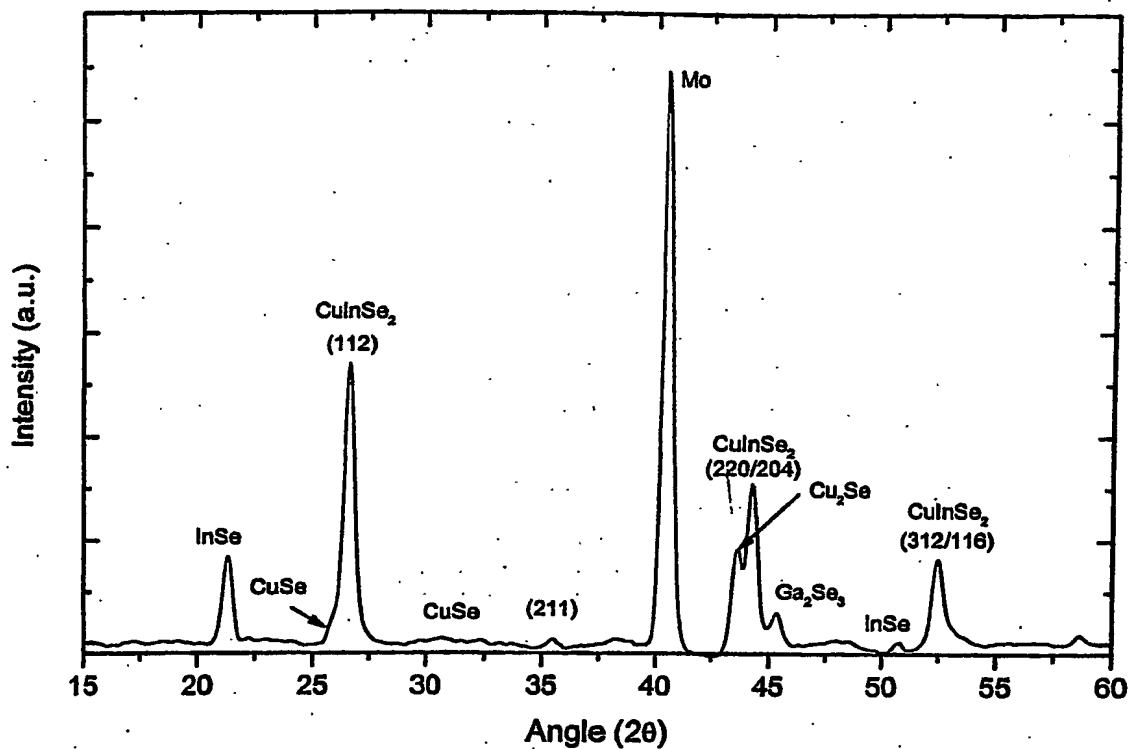


Figure 1.2

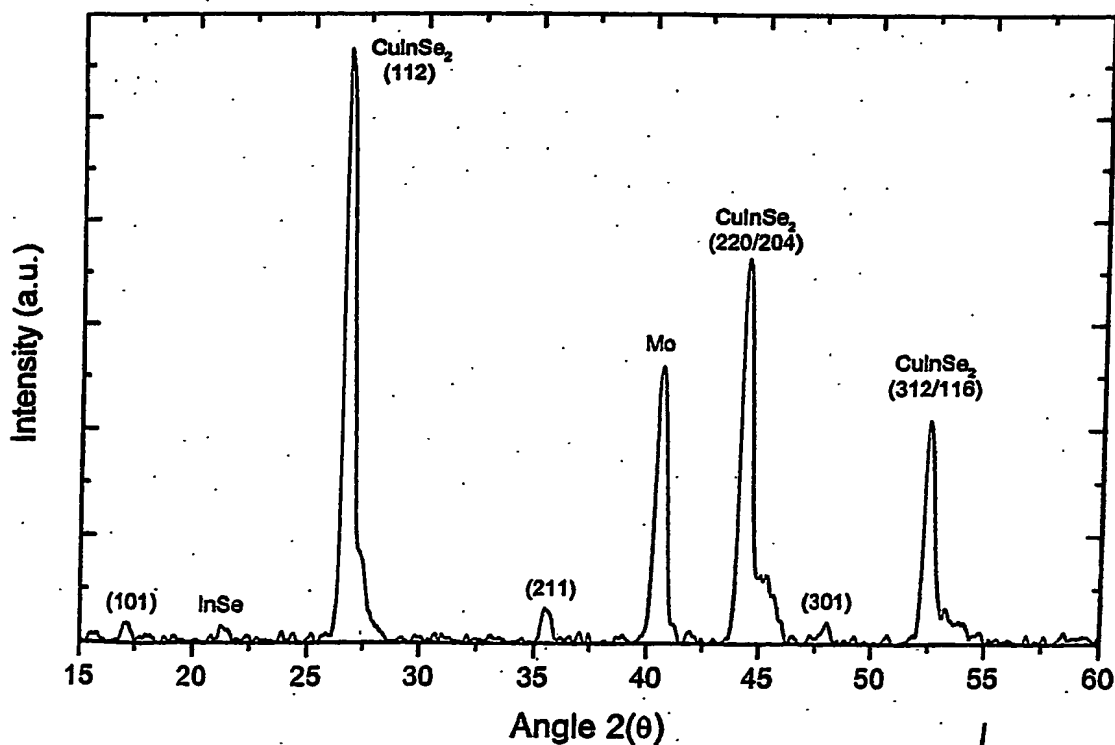


Figure 2

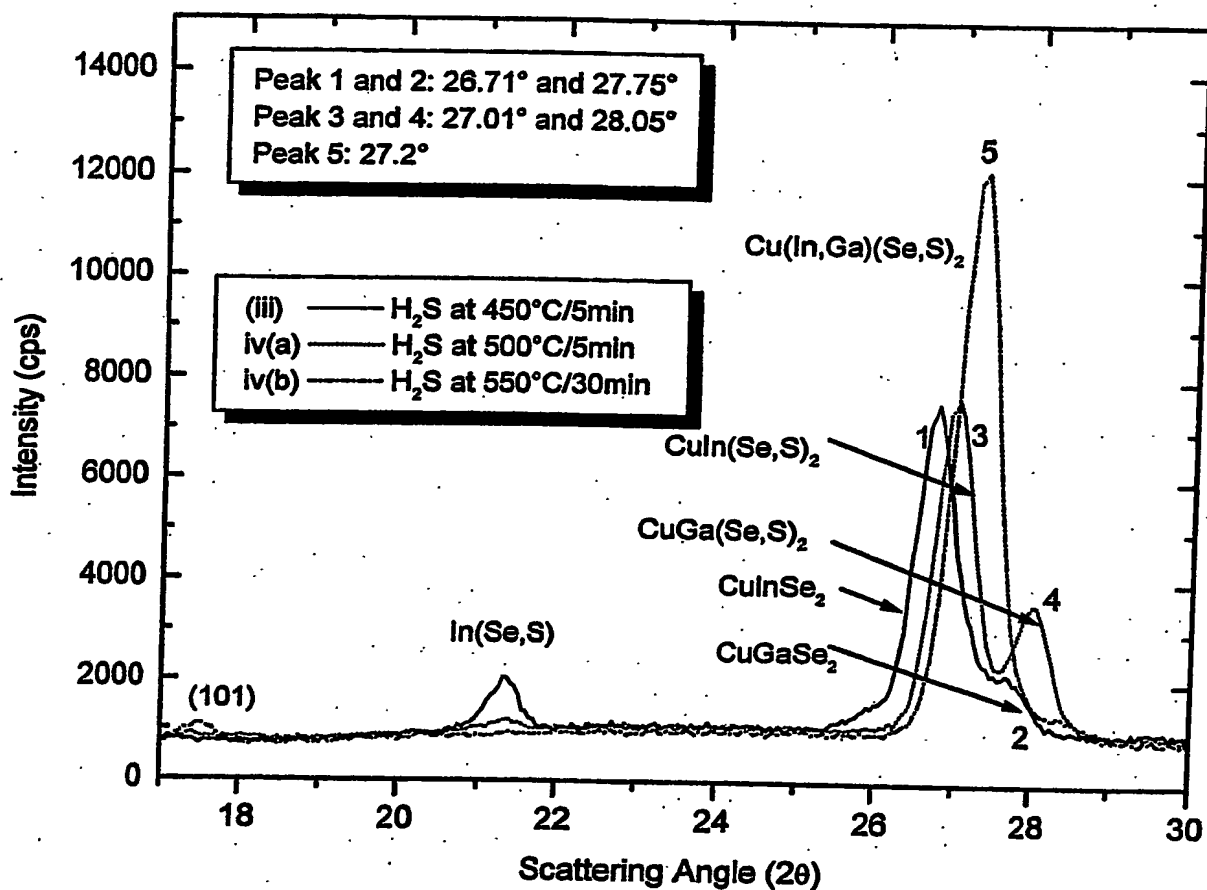


Figure 3.1

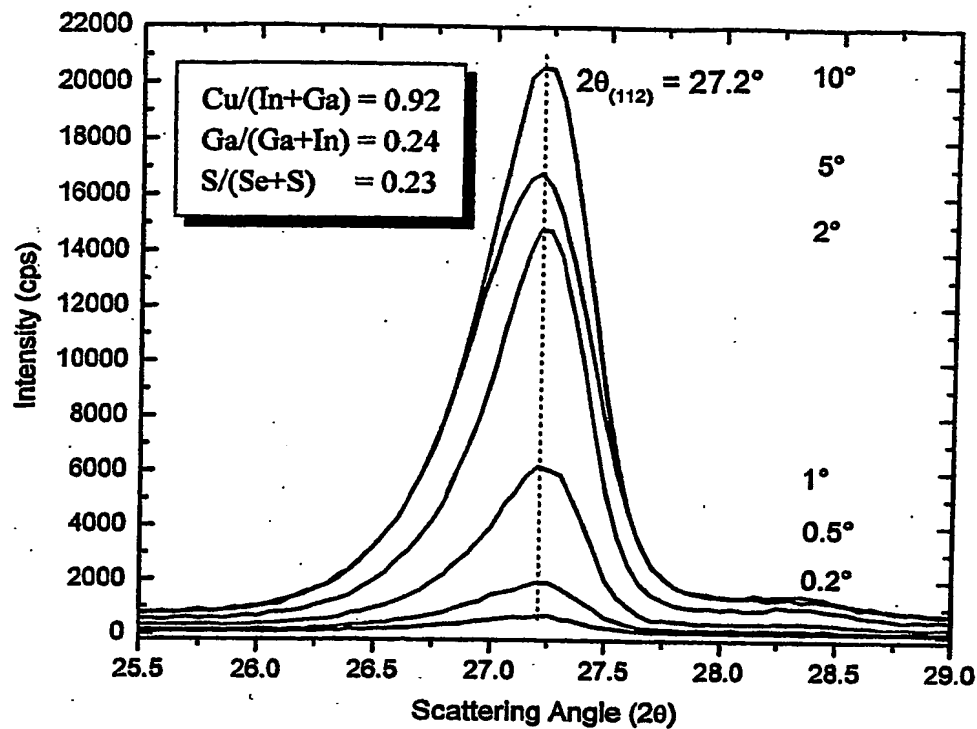


Figure 3.2

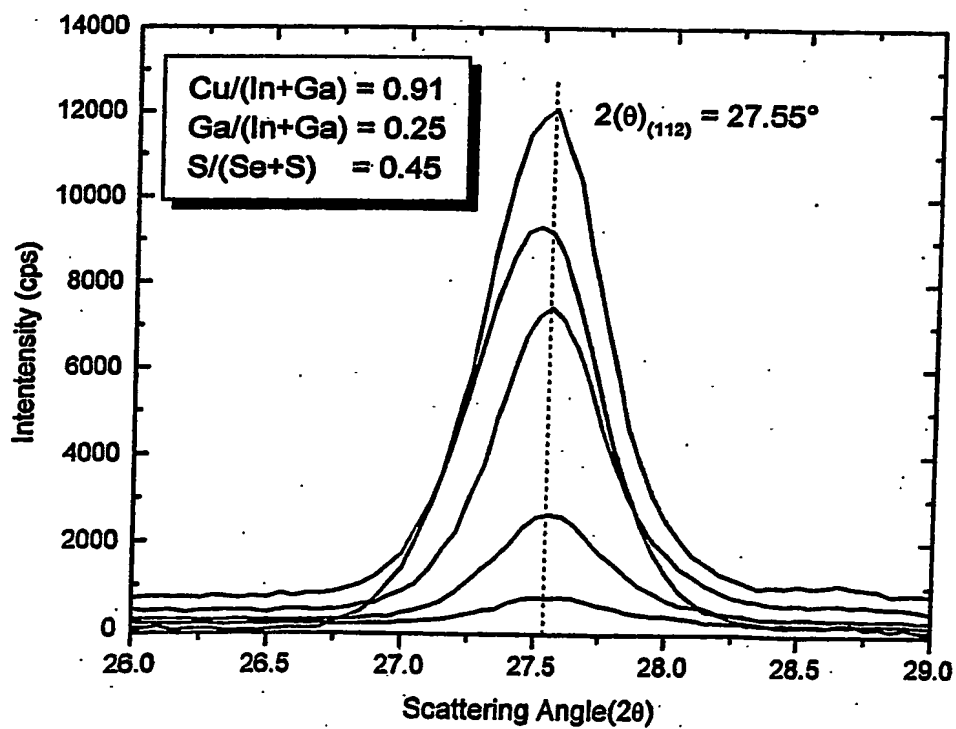


Figure 4

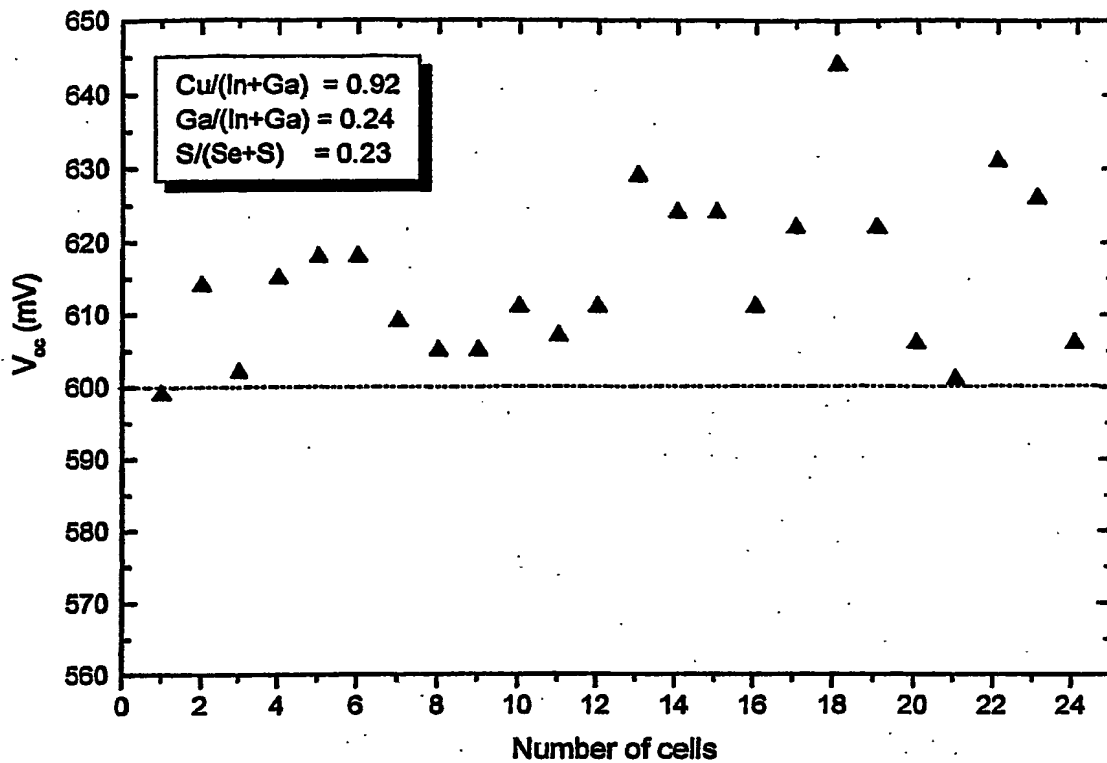


Figure 5

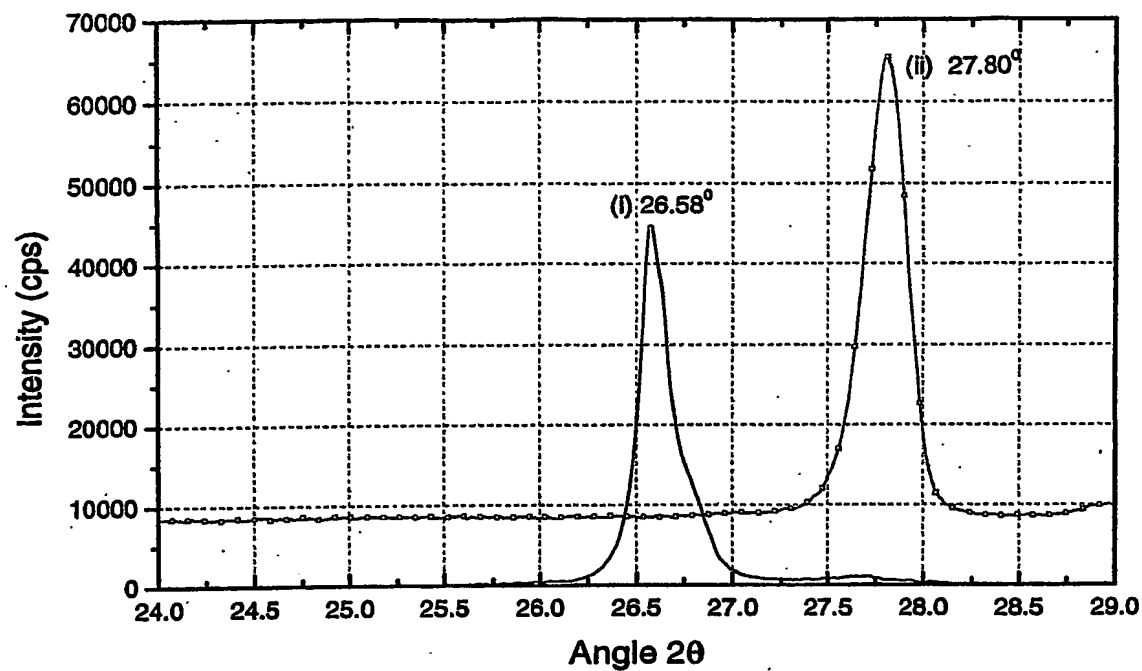




Figure 6

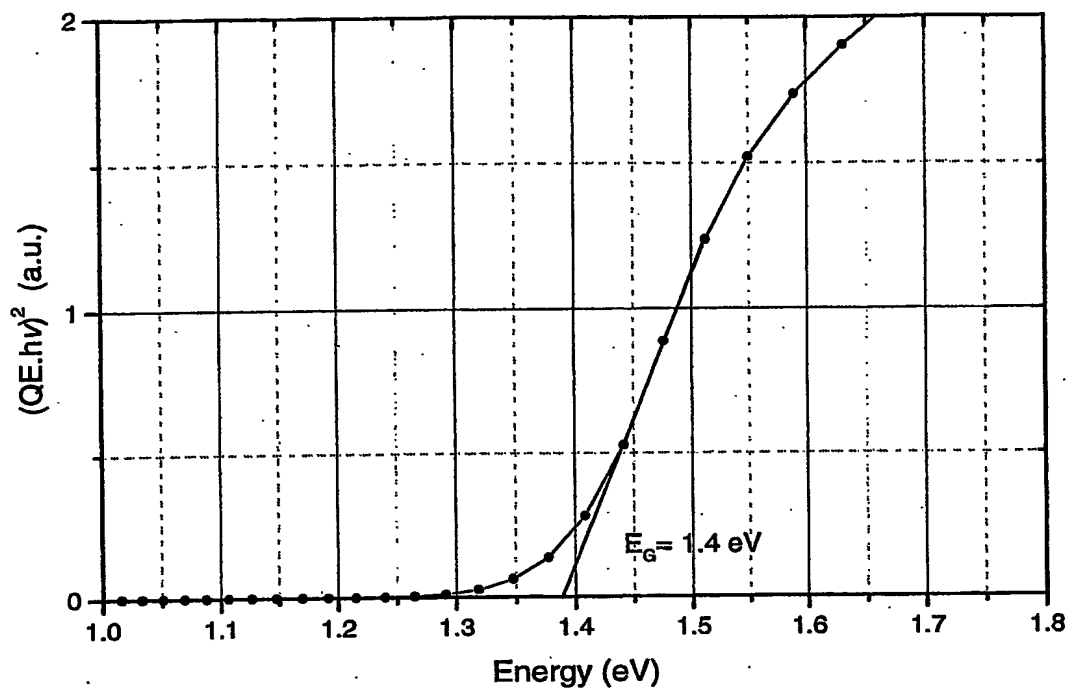


Figure 7

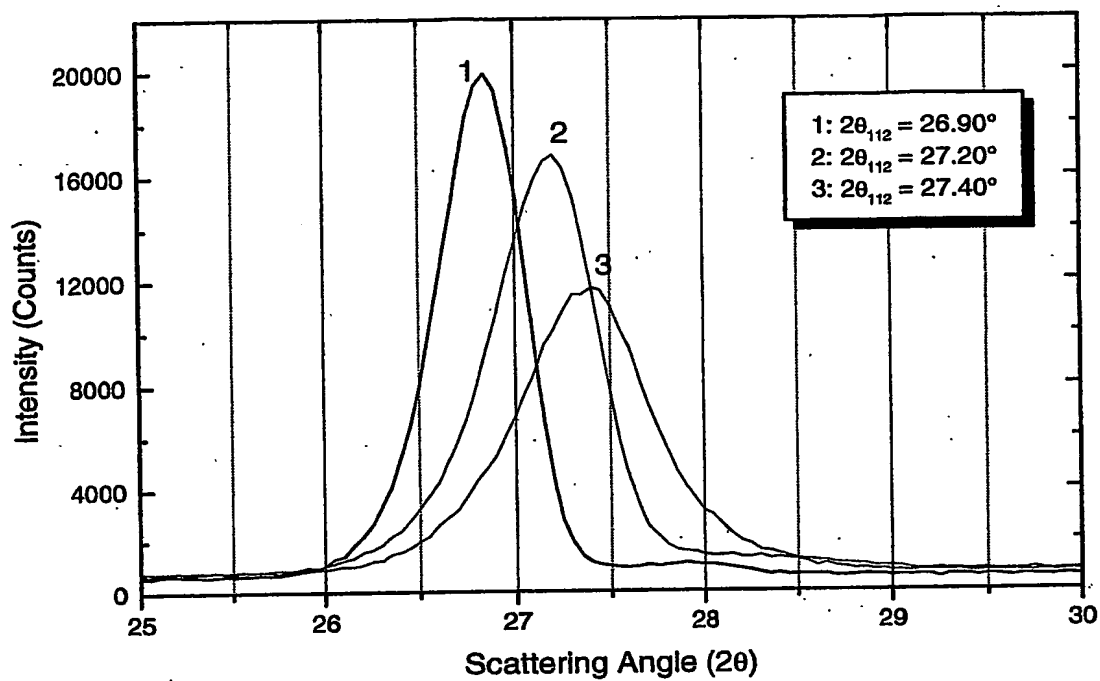


Figure 8

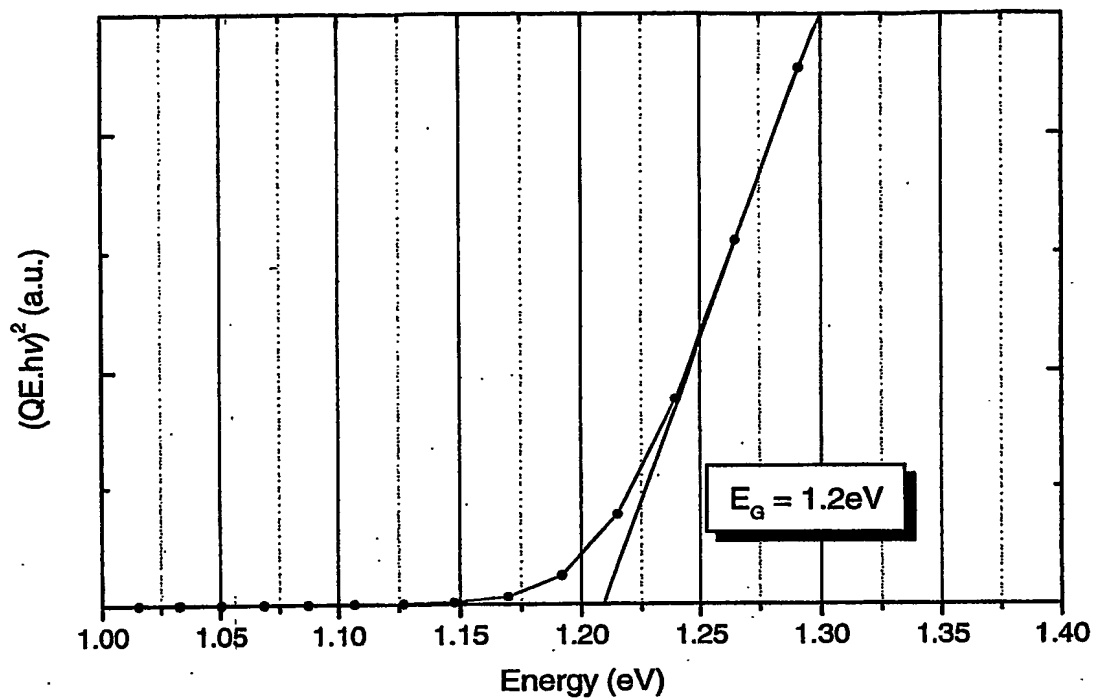


Figure 9

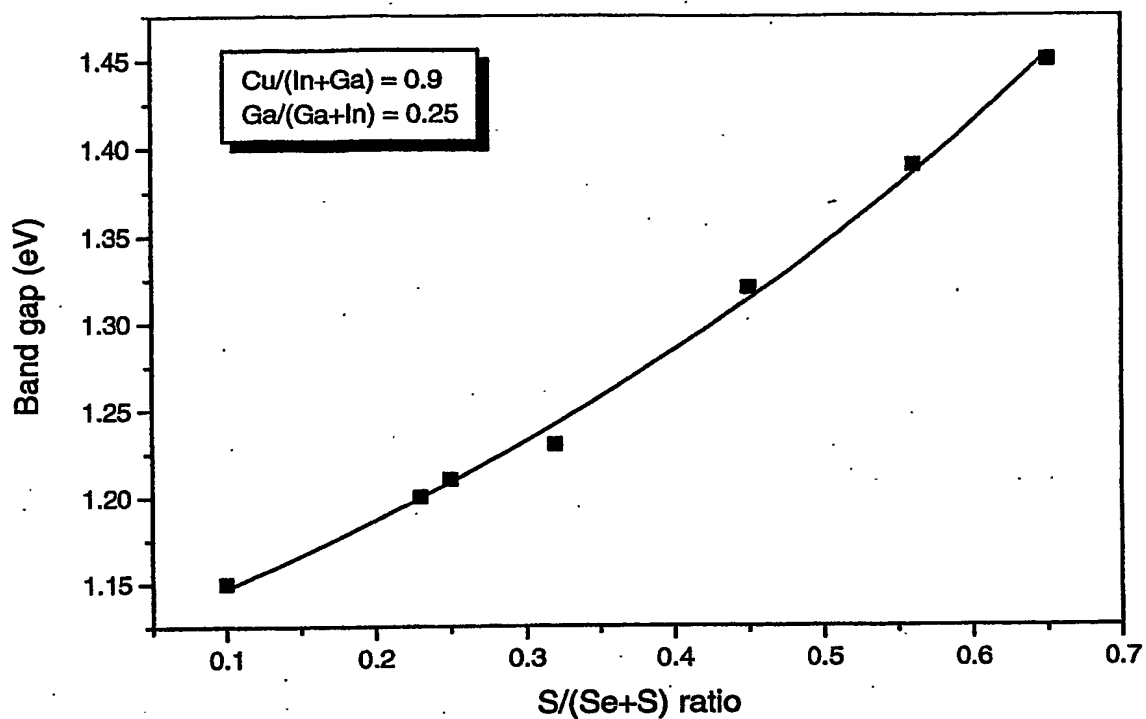


Figure 10

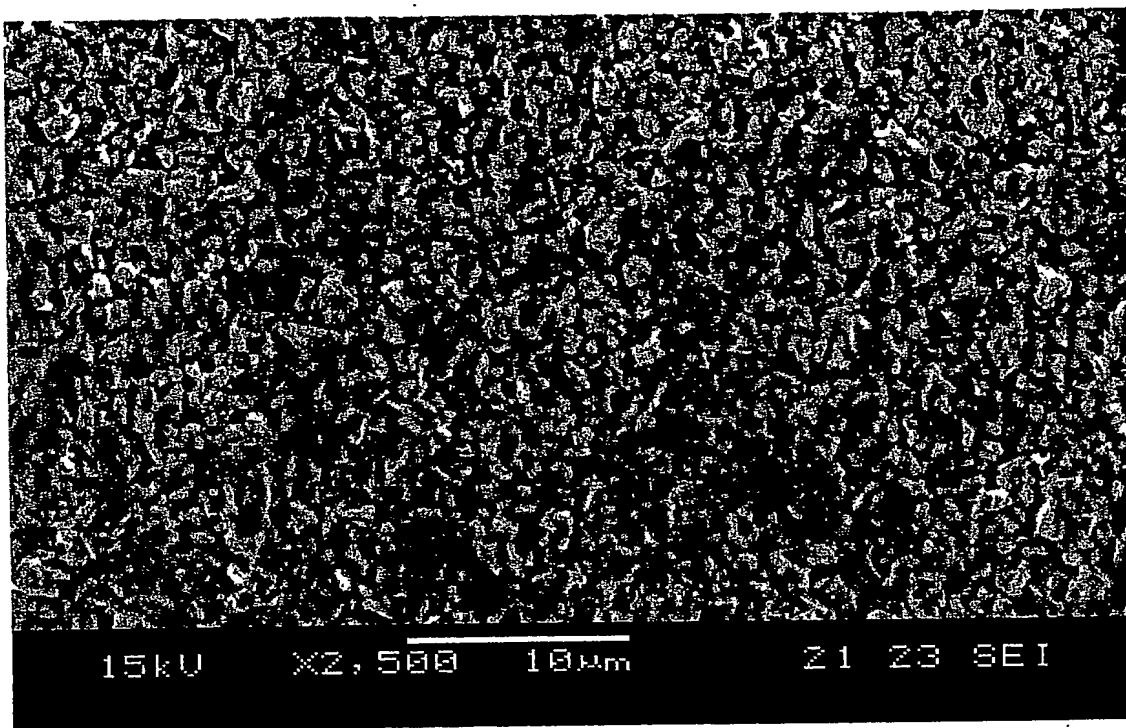


Figure 11

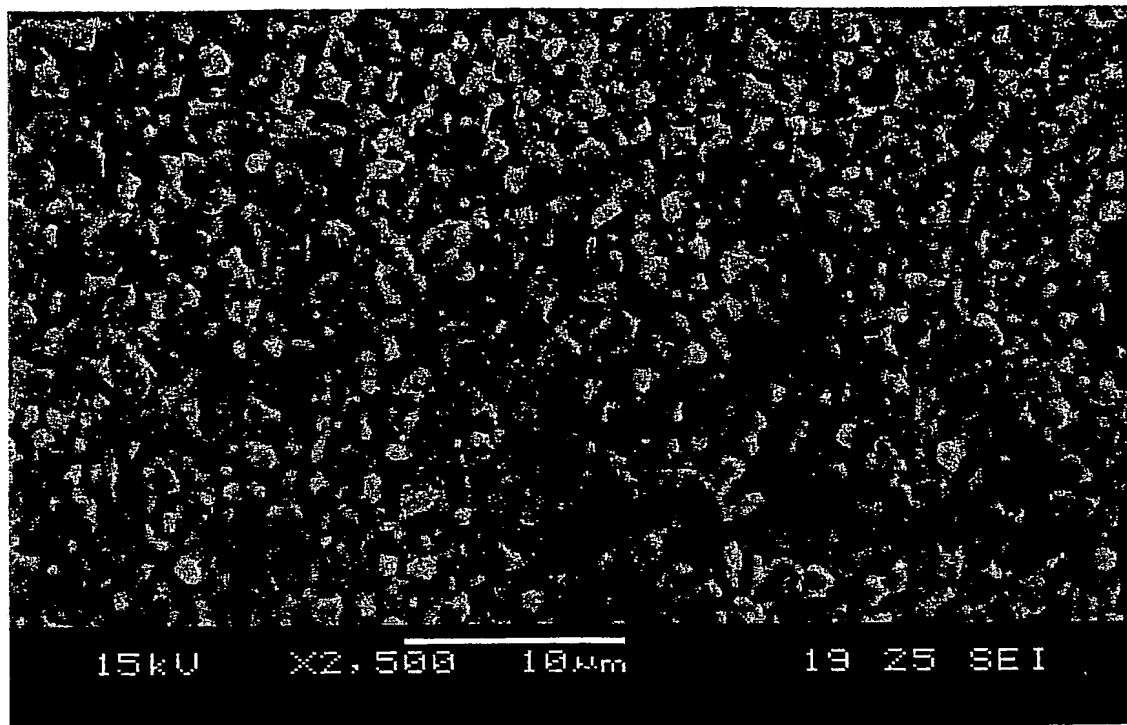


Figure 12

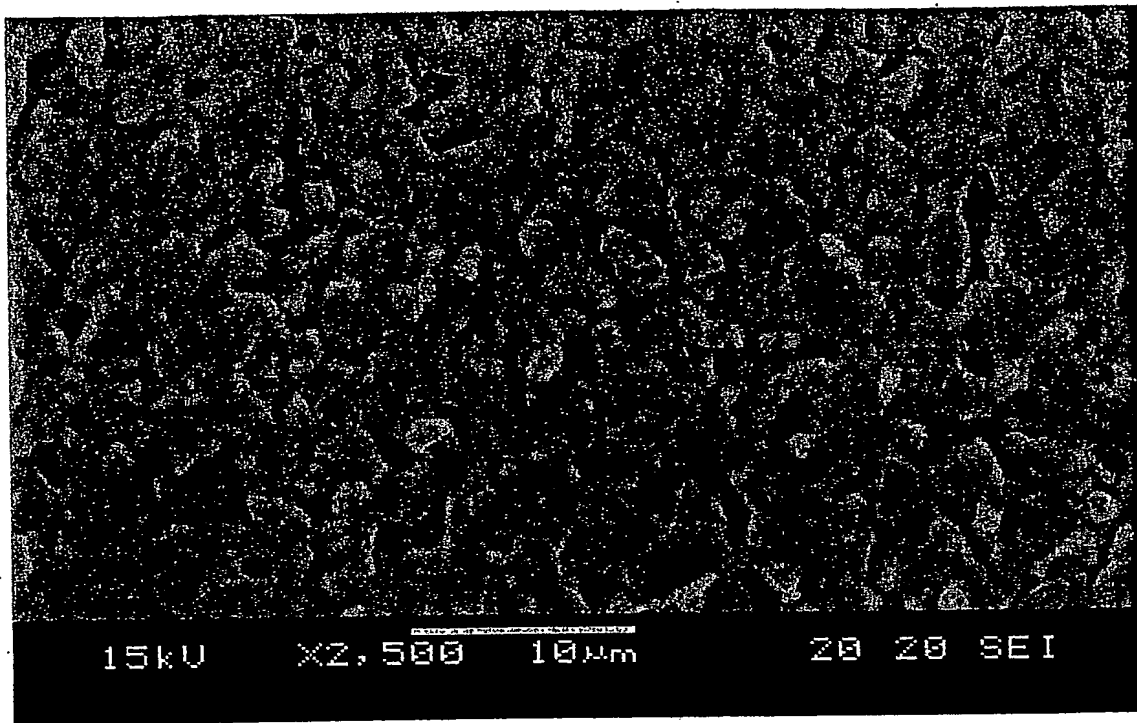


Figure 13.1

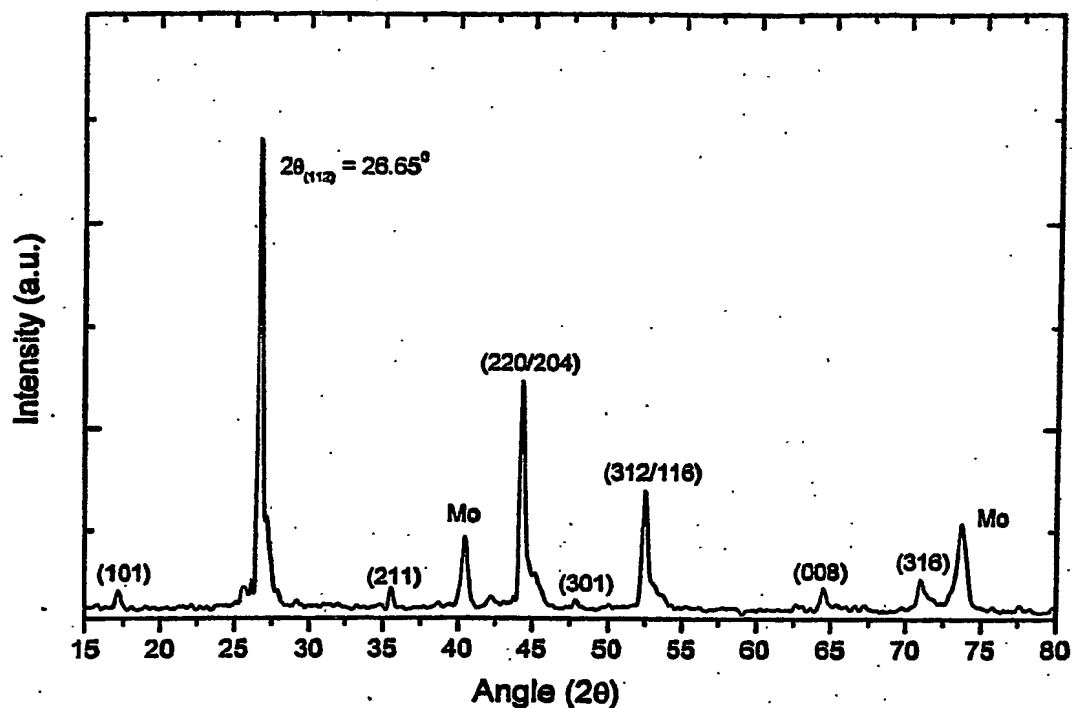


Figure 13.2

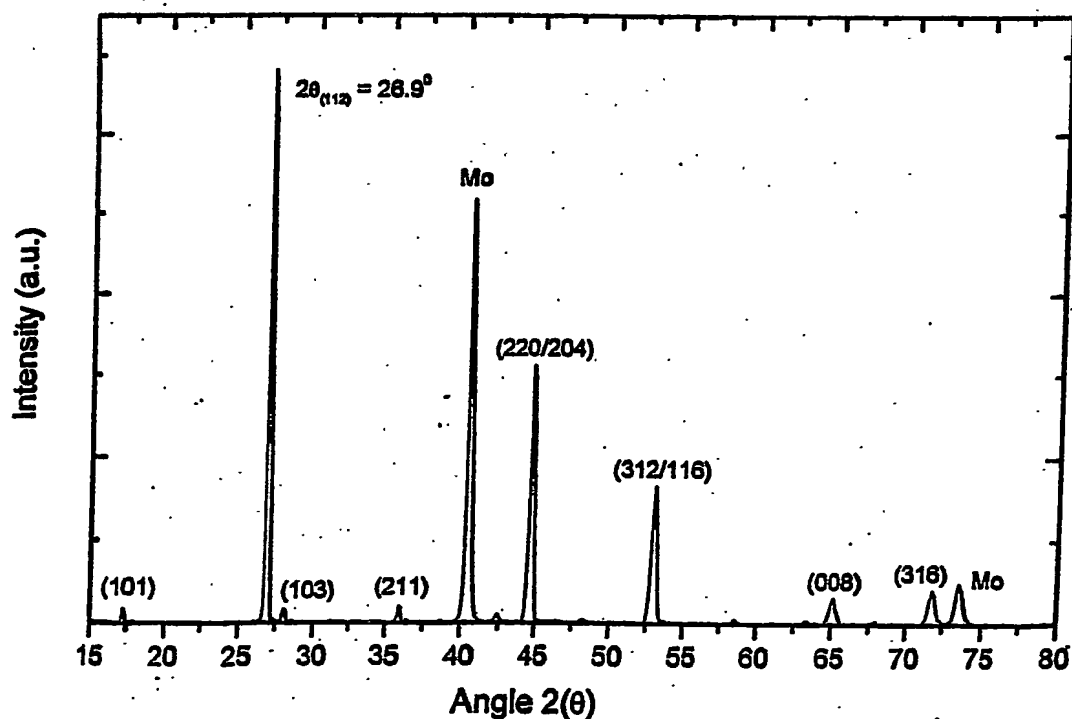




Figure 14

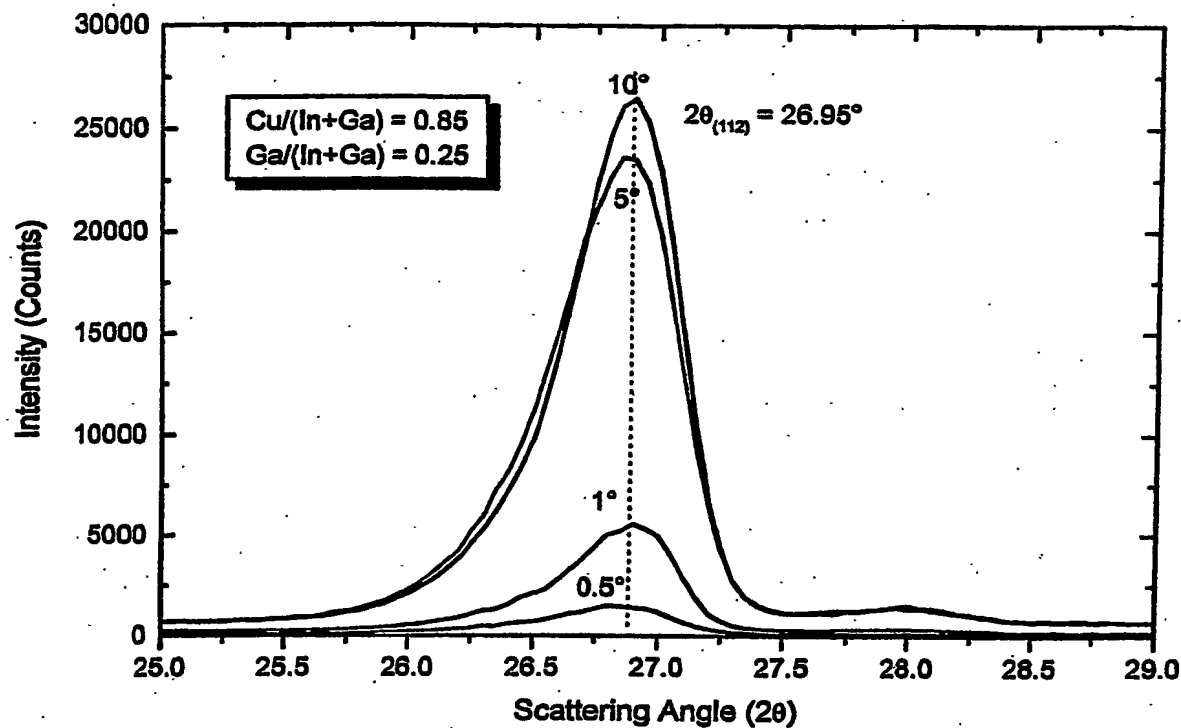


Figure 15.1

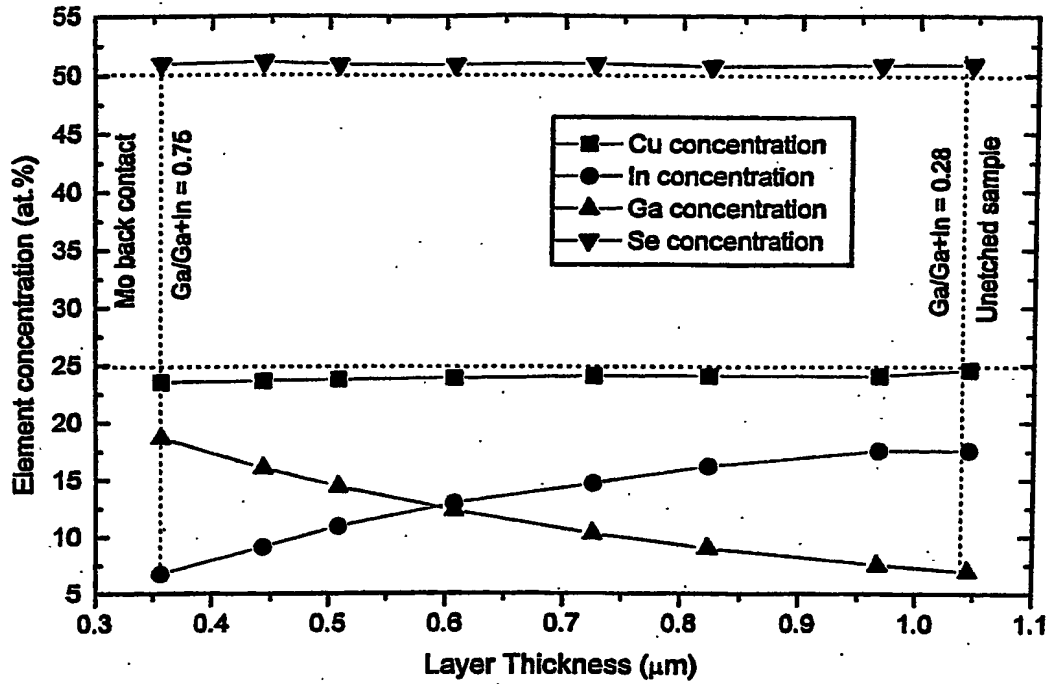
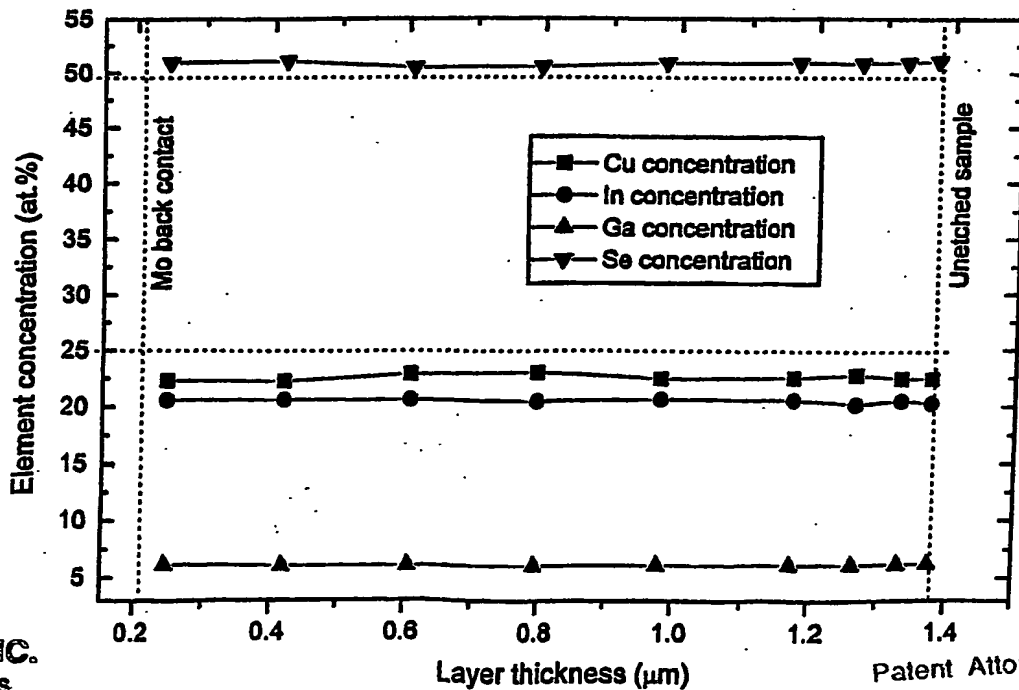


Figure 15.2



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